

## Catalytical Photocyclization of Arylamines with $\alpha$ -olefins in the Synthesis of 2-Alkylquinoline

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### ABSTRACT

The article deals with the results of investigation of the process of catalytical photocyclization of aniline and aniline hydrochloride with  $\alpha$ -olefins (hexene-1, heptene-1 and octene-1). The following compounds of d- and f-metals are tested as probable catalysts: CuSO<sub>4</sub>•5H<sub>2</sub>O, EuCl<sub>3</sub>•6H<sub>2</sub>O, PrCl<sub>3</sub>•6H<sub>2</sub>O, TbCl<sub>3</sub>•6H<sub>2</sub>O, La<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, NiSO<sub>4</sub>•6H<sub>2</sub>O, NiCl<sub>2</sub>•6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, [Ni(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>NiCl<sub>2</sub>. Catalytic effect in the reaction of photocyclization is only detected for nickel compounds. The products of catalytical photocyclization are 2-alkylquinolines. Maximum output is observed for 2-propylquinoline and is equal to 45 % at conversion of aniline of 57 %. Photosynthesis of quinolinic bases proceeds under the influence of UV-radiation at room temperature. Catalytical activity of nickel ions in a series of investigated compounds marginally depends on ligand environment. The influence of solvents' nature on the efficiency of catalytical photocyclization is detected. The output of the target product decreased in the following series: EtOH > DMSO > DMFA > Toluol > Hexane > solventless system. Catalytical photocyclization of hydrochloride aniline with  $\alpha$ -olefine in water environment relates to ecologically friendly way of 2-alkylquinolines synthesis.

### KEYWORDS

Photocyclization, catalysis, aniline, aniline hydrochloride, alkene, 2-alkylquinoline

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## Introduction

Quinolinic bases are widely applied in pharmacy as active constituents in the medical products with antimalarial, antibacterial, antidiabetic and anti-inflammatory activity (Soldatenkov, Koljadina & Shendrik, 2001; Jenekhe, Lu & Alam, 2001; Liu, Tang & Zeng, 2016; Zeng & Zhou, 2016). The materials on the basis of polyquinolines synthesized from substituted quinolone bases are

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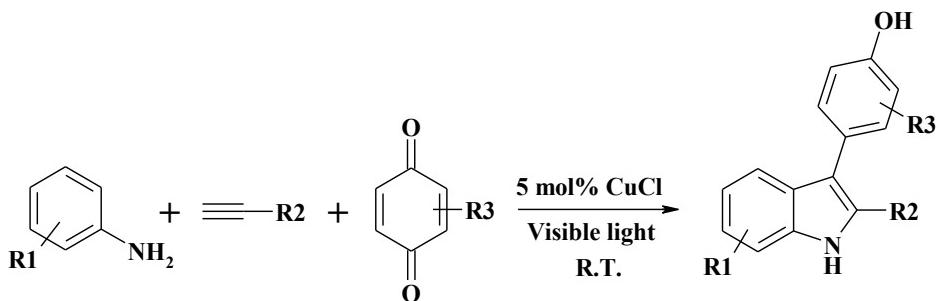
promising for creation of composite and electroluminescent structures (Rusanov et al., 2005), nano- and meso-structural compounds for organic electronics and nonlinear optics (García-López, Çetin & Greaney, 2015; Gulevich et al., 2012; Sarkar et al., 2015). Some derivatives of quinolines are antioxidants (age resistors) of rubber and inhibitors of corrosion, and are consisted in cyanine dyes, extractants and sorbents (Biswas & Greaney, 2011; Li & Shi, 2016; Pintori & Greaney, 2011).

There are the methods of traditional synthesis of quinolinic nitroheterocyclic compounds (Selimov, Ptashko & Dzhemilev, 2002) and modern methods with the application of metal complex catalysts (Bulgakov et al., 2005).

In our laboratory we developed a brand new way of synthesis of alkyl-substituted quinolines by means of catalytical photocyclization (Mahmutov et al., 2016a; 2016b).

Photocatalytic transformations are of particular interest both for the science and for the practice. The most significant of them is the process of photosynthesis. The possibility of reacting under exposure to light, for example, photocatalytical destruction of water by sunlight, is one of the hottest issues of the modern times (Corrigan et al., 2016; Huang, et al., 2016; Martin, 2015; Parasram, Iaroshenko & Gevorgyan, 2014; Parasram et al., 2016).

The first example of successful photocatalytical synthesis of nitroheterocyclic compounds is the work by A. Sagadevan, A. Ragupathi & K.C. Hwang (2015). According to the authors, they managed to perform a unique reaction of synthesis of complex indole by means of catalytical photocyclization of arylamines and terminal alkynes with quinone (Figure 1).



**Figure 1.** The Scheme of Catalytical Photocyclization of Arylamines and Terminal Alkine Benzoquinone

Detected reaction of photocyclization is catalyzed by copper chloride (I) during exposure to visible light at room temperature.

The research of catalytical photocyclization of arylamines with  $\alpha$ -olefine for direct synthesis of 2-alkylquinolines was the objective of our work. As a model system we chose the following reaction mixture: Aniline – Hexene-1 – EtOH. As catalysts we tested the following compounds of d- and f-metals: CuSO<sub>4</sub> · 5H<sub>2</sub>O, EuCl<sub>3</sub> · 6H<sub>2</sub>O, PrCl<sub>3</sub> · 6H<sub>2</sub>O, TbCl<sub>3</sub> · 6H<sub>2</sub>O, La<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, NiSO<sub>4</sub> · 6H<sub>2</sub>O, NiCl<sub>2</sub> · 6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, [Ni(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]₂NiCl<sub>2</sub>.

Influence of the solvent nature on the process of catalytical photocyclization is considered with the examples of various types of solvents: bipolar, polar and apolar. The main emphasis is laid on the choice of the water environment which

is preconditioned by the availability and cheapness of such solvent as water. Besides, the synthesis in water environment is more ecologically friendly in comparison with the application of toxic solvents.

### **Experimental Part**

The researches were conducted in the physical and chemical testing laboratory of the Birsk Branch of the Bashkir State University.

Catalytical photocyclization was carried out in a photocatalytical apparatus Photo Catalytic Reactor Lelesil Innovative Systems with silica reactor having the capacity of 250 ml (photoreactor of Stromeyer's type with magnetic stir bar).

Original reagents (aniline, hexene-1, heptene-1, octene-1), catalysts ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{La}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and solvents (EtOH, DMSO, DMFA, Toluol, Hexane) are CP (chemically pure) commercial products.

Ammoniac complex  $[\text{Ni}(\text{NH}_3)_4]\text{Cl}_2$  is synthesized in accordance with the methods (Koldica, 1984) Triphenylphosphinic complex  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NiCl}_2$  is synthesized in glacial acetic acid in accordance with the methods (Experiment 3, 2013).

Hydrochloride aniline (phenylammonium chloride,  $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$ ) is synthesized in accordance with the well-known methods based on the reaction of aniline with the concentrated chlorine hydride (Agranomov, 1974).

Preparation of catalysts and conduction of the process of catalytical photocyclization were performed according to the methods described in (Mahmutov et al., 2016a).

The source of ultraviolet emission was DRT-125-1 low-pressure mercury-vapor lamp. The sphere of spectral range is 230 – 400 nm at the maximum at 315 nm. Nominal light flow is 1850 lm. Ultraviolet emission reaches the reaction environment passing through the water layer. The temperature of the thermostat is 20 °C. The time of conduction of the catalytical photocyclization process is 6 hours.

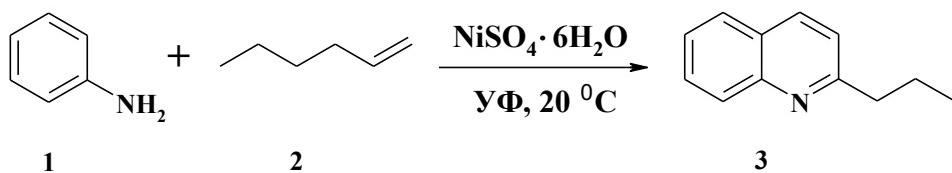
For identification of the structure of the reaction products we used SHIMADZU GCMS-QP2010S gas chromatograph/mass spectrometer.

### **Evaluation**

Based on the results of the conducted researches we discovered that catalytical activity in the reaction of photocyclization of aniline (1) with hexeneom-1 (2) is peculiar only to nickel compounds. Catalytical activity of the other tested compounds such as:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{La}_2\text{O}_3$  and  $\text{MnO}_2$  in reaction of photocyclization is not found.

According to the data of the chromato/mass spectral analysis the main product of catalytical photocyclization in the model system of Aniline – Hexene-1 – EtOH is 2-propylquinoline (3).

General scheme of reaction of catalytical photocyclization 1 and 2 under the influence of nickel catalyst may be represented as follows (Figure 2).



**Figure 2.** Scheme of Catalytical Photocyclization of Aniline with Hexene-1,  $\text{Y}\Phi = \text{UV}$

Output of main product 3, according to the results of initial vacuum fractionating is equal to 45% at conversion 2 – 57 %. In the trace amounts we found the products of oxidation 2 – 2-hexene-1-ol and 2-hexaneal. These substances are probably possible intermediates of the photocyclization reaction. Elaborate study of the reaction mechanism is the subject to further investigation.

Catalytical activity of nickel compounds in the model system: Aniline – Hexene-1 – EtOH on the output of target product 3 is represented in table 1.

**Table 1.** Catalytical Activity of Nickel Compounds in Reaction of Photocyclization of Aniline with Hexene-1

No	Catalyst	Output of 2-propylquinoline, %	Conversion of Aniline, %
1	NiCl <sub>2</sub> ·6H <sub>2</sub> O	48	57
2	NiSO <sub>4</sub> ·6H <sub>2</sub> O	42	57
3	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	40	55
4	[Ni(NH <sub>3</sub> ) <sub>4</sub> ]Cl <sub>2</sub>	37	44
5	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P] <sub>2</sub> NiCl <sub>2</sub>	31	36
6	without catalyst	0	0

We detected that the highest output of 2-propylquinoline is observed in case of nickel dichloride (table No.1, p. 1), which is highly soluble in reaction environment, i.e. catalytical reaction of photocyclization proceeds in homogenous system. However, we found no significant influence on the output of product 3 in the investigated series of nickel crystallohydrate (table No.1, p. 1-3).

In case of nickel ammine (table No.1, p. 4) and nickel (II) dichloride-bis-triphenylphosphine (table No.1, p. 5) one observes low output of target product 3. In the absence of catalyst (table No.1, p. 6) there is no photocyclization of 1 and 2.

We studied the influence of the solvent nature on the output of substituted quinoline 3. The results are represented in table 2.

**Table 2.** Influence of Solvent on Catalytical Photocyclization of Aniline with Hexeneom-1 (Catalyst NiCl<sub>2</sub>·6H<sub>2</sub>O)

No	Solvent	Output of 2-propylquinoline, %	Conversion of Aniline, %
1	EtOH	48	57
2	DMSO	44	59
3	DMFA	39	50
4	Toluol	23	12
5	Hexane	20	14
6	without solvent	15	19

The highest output of product 3 and conversion of initial 1 is observed at conduction of the reaction in ethanol and DMSO, while the lowest one is in apolar solvents.

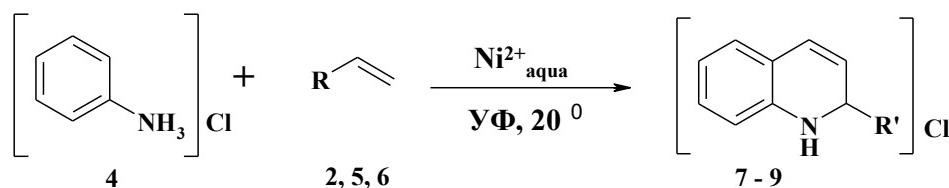
Influence of polar solvents EtOH > DMSO > DMFA on catalytic effect is probably connected with presence of electrodonor centers (according to Pearson's classification) (Pearson, 1971). In the effective solvents there is only one such center – atom O, while in less effective DMFA there are two centers: atoms N and O.

In apolar solvents decrease in output and conversion is first connected with the disturbance of the system homogeneity. In the absence of solvent the reaction mass becomes resinified turning into the viscous mass and the general catalytic effect thus significantly decreases the output of the target product.

With the purpose of synthesis of 2-alkyl-substituted quinolines in water environment we studied catalytical photocyclization of water-soluble hydrochloride aniline (4) with alkenes: hexene-1 (2), heptene-1 (5) and octene-1 (6). As catalyst we applied crystallohydrates of nickel salts:  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

The main photochemical reaction proceeds in the boundary of two liquid phases, because the reaction system is initially heterogeneous. Lower reaction layer is water solution of nickel salts and hydrochloride aniline, and the upper organic layer is the corresponding liquid alkene. The moment of the end of the process of catalytical photocyclization is clearly seen as the upper organic phase is disappearing. In the average the consumption of alkene in the chemical reaction lasts for 6-8 hours. This phenomenon will probably be used for investigation of kinetics of the catalytical photocyclization process.

The main photochemical process proceeds according to figure 3 with formation of water soluble hydrochloride 2-alkylquinoline 7-9.



**Figure 3.** Catalytical Photocyclization of Hydrochloride Aniline with Alkenes:  
 $\text{R} = \text{C}_4\text{H}_9$ - (2),  $\text{C}_5\text{H}_{11}$ - (5) and  $\text{C}_6\text{H}_{13}$ - (6);  $\text{R}' = \text{C}_3\text{H}_7$ - (7),  $\text{C}_4\text{H}_9$ - (8) and  $\text{C}_5\text{H}_{11}$ - (9),  $\text{Y}\Phi = \text{UV}$

The synthesized 2-alkyl-substituted quinolines 2-propylquinoline (3), 2-butylquinoline (10) and 2-amylquinoline (11) were extracted from the reaction mixture according to the reaction of neutralization with 20% sodium carbonate solution. The output of reaction products 3, 10 and 11 according to the results of the initial vacuum fractionating is represented in table 3.

**Table 3.** Output of Substituted Quinolones at Catalytical Photocyclization of Hydrochloride Aniline with Alkenes in Water Environment(Catalyst -  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ )

No	Alkene	Product of Photocyclization	Output of Product, %
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1	Hexene-1 (2)		36
<hr/>			
2	Heptene-1 (5)		31
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3	Octene-1 (6)		24

The highest output is observed at the synthesis of product 3 – 36%, while the lowest – 24% for product 11. Thus the output of the photocyclization product decreases with the increase in the length of hydrocarbyl alkene.

We studied the influence of catalyst's nature, i.e. ligand environment of nickel ion on output 3 in water environment. The results are represented in table 4.

**Table 4.** Influence of Catalyst's Nature on the Output of 2-Propylquinoline in Water Environment

No	Catalyst	Output of 2- propylquinoline, %
1	NiCl <sub>2</sub>	36
2	NiSO <sub>4</sub>	34
3	Ni(NO <sub>3</sub> ) <sub>2</sub>	31
4	without catalyst	0

## Conclusions

We found that the studied series of nickel ions salts in water environment have no significant influence on the output of product 3. It is probably connected with formation of stable hydrated complexes of nickel ions in water solution free from the ligand influence of salt-forming ions. In the absence of catalyst there is no reaction between photocyclization hydrochloride aniline and hexene-1.

The studied photosynthesis of 2-alkyl-substituted quinolines in water environment is acceptable and ecologically friendly way of synthesis of substituted quinolines.

Thus, we found and studied a new way of synthesis of 2-alkylquinolines in catalytical reaction of arylamines with  $\alpha$ -olefines, proceeding according to photocyclization type during exposure to ultraviolet light. The catalysts of photocyclization are available crystallohydrates of nickel salts.

## Disclosure statement

No potential conflict of interest was reported by the authors.

### Notes on contributors

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